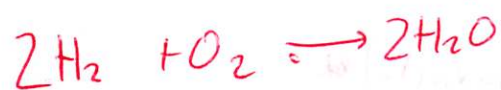


# Ch 13 Equilibrium

Chemical Equilibrium - dynamic state where the  $[ ]$ 's of Reactants + Products are const. w/ time

Any Rxn in closed container will Reach Equilibrium

Some Rxns ~~are~~ do not appear Reversible

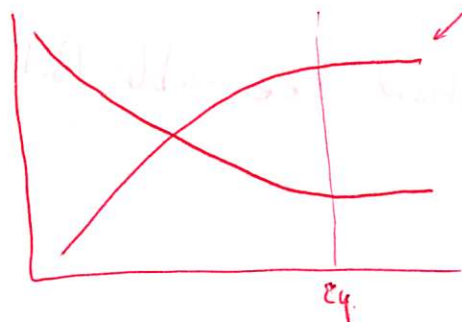


or not React @ all



13.1 Equilibrium is dynamic

Flow of traffic across a bridge B/w 2 islands



✓  $[ ]$  constant @ Eq.

as the  $[\text{product}] \uparrow$  the Forward Rxn slows  $\downarrow$  and the Rev Rate  $\uparrow$

Eventually the 2 Rates are =

The position of  $E_q$  depends on  $[J]_0, E, S,$

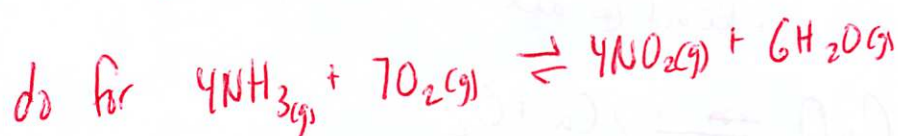
How do we study the  $E_q$  Constant

1864 law of mass action  $\rightarrow$  describes the  $E_q$  situation



$$K = \frac{[C]^e [D]^m}{[A]^j [B]^k} \quad \text{equilibrium expression}$$

$E_q$  Constant (no units)



~~K~~

Do Exercise 13.1 w/  $\text{NH}_3$

talk about how exponents may D B/c of coefficients ~~10/10~~ Thus  
K D's BUT the proportion is the same. So everything works out.

@ given T K is constant. See table 13.1

13.3  $K_p$   $\text{D}$

2

Can do Equilibrium Expression w/ Pressure

$$PV = nRT \rightarrow P = \frac{nRT}{V} \rightarrow P = \underset{\substack{\uparrow \\ [M]}}{C} RT$$

So we can sub in P for [ ]

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(C_{NH_3})^2}{(C_{N_2})(C_{H_2})^3} = K_c \leftarrow C = \text{concentration}$$

for pressure

$$K_p = \frac{P_{NH_3}^2}{(P_{N_2})(P_{H_2})^3}$$

Pressure

Thus  $K \propto K_p$

But Not out & Dry

watch



$$K = \frac{[HF]^2}{[H_2][F_2]} = \frac{C_{HF}^2}{C_{H_2} C_{F_2}}$$

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{C_{NH_3}^2}{C_{N_2} C_{H_2}^3}$$

BUT

$$\text{Since } C = \frac{P}{RT} \quad \frac{\left(\frac{P_{NH_3}}{RT}\right)^2}{\left(\frac{P_{N_2}}{RT}\right)\left(\frac{P_{H_2}}{RT}\right)^3} = \frac{P_{NH_3}^2}{(P_{N_2})(P_{H_2})^3} = \frac{\left(\frac{1}{RT}\right)^2}{\left(\frac{1}{RT}\right)^4}$$

$$= \frac{\left(\frac{P_{HF}}{RT}\right)^2}{\left(\frac{P_{H_2}}{RT}\right)\left(\frac{P_{F_2}}{RT}\right)} = \frac{(P_{HF})^2}{(P_{H_2})(P_{F_2})}$$

$$K = K_p$$

$$S. K = K_p (RT)^4 \quad \frac{P_{NH_3}^2}{(P_{N_2})(P_{H_2})^3} (RT)^2 = \cancel{K_p} RT$$

So  $K_p \propto K_c$  is dependency on  $R$  and  $n$

Thus  $\boxed{K_p = K (RT)^{\Delta n}}$

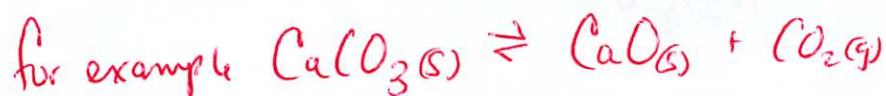
$\uparrow$   
 Ideal

$\Delta n = \text{moles}_{\text{prod}} - \text{moles}_{\text{react}}$

13.5

### 13.4 Heterogeneous Eq

Solids + liquids are Not in  $K_c$  expression



Normally  $K = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]}$  But  $[\text{Solid}]$  doesn't change  
 so it is not entered into the  
 Equilibrium Expression

$\frac{\text{Mol}}{L} = \frac{\frac{g}{L}}{\frac{g}{\text{mol}}}$

$\leftarrow$  solid/liq constant @ given  $T$   
 $\leftarrow$  always constant.

} these these  
do not affect  $K$

also these  $H$ 's are very large and  
 would not have (-) effect on  $K$

So

$K = [\text{CO}_2]$



### 13.5 Applications of K

3

pg 591-592 Not going into

What K can determine

Extent of a Rxn

If  $K$  is big Products favored Rxn goes to near completion

$K$  is small Reactants favored like weak acids

Size of  $K$  is not directly related to time to reach Eq

Fig 13.7

Rate or size of  $E_a$

↑  
 $K$  depends on Thermodynamics ( $\Delta H$ ) (Ch 16)

Reaction Quotient  $\rightarrow$  Used to see if a Rxn in Eq

$Q =$  same expression as  $K$

$$Q = \frac{[C]_0^c [D]_0^d}{[A]_0^a [B]_0^b} \quad \text{but using } [ ]_0 \leftarrow \text{initial}$$

if  $Q = K @ E_q$

$Q > K$  not in  $E_q$  will shift Left to reach  $E_q$

$Q < K$  not in  $E_q$  will shift Right

$E_q$  Calc simple

given  $K$  solve for Reactant/Product  $[ ]$

or like Prob 13.9 page 595

asked to find  $[E_q]$ 's use ICE Box

Sample 13.10, 13.11 do out. (No Quadratic)

Sample 13.12 will use quadratic

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

although when small  $K$  assume  $x$  is very small

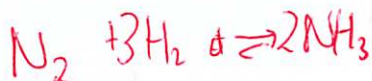
13.7 & Chatelier's Principle - if an  $E_q$  is stressed/change of the  $E_q$  will shift to Relieve that stress/change

See table 13.2 to show  $[H_2O]$  changes w/ Temp/P

So if a component entered the  $E_q$  shifts to consume that component

If it was taken away, the  $E_q$  shifts to make more of that component.

Can show this w/  $Q$



@  $E_q$   $[N_2] = 0.399 M$   
 $[H_2] = 1.197 M$   
 $[NH_3] = 0.202$

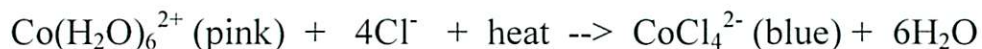
∴ Ineq  $N_2$  added.

How will  $E_q$  shift. Use  $Q$

## Cobalt Chloride Demo

If you google cobalt chloride equilibrium, you'll find quite a few lab procedures. The reason for dissolving the cobalt chloride in the ethanol is to show the color of the  $\text{CoCl}_4^{2-}$  complex.

I did this as a demo without the ethanol. The equilibrium you're looking at is:



I made 0.1M  $\text{CoCl}_2$  before hand. 0.714g in 30 mL soln

1. Fill a test tube about 3/4 full with  $\text{CoCl}_2$  (pink).
2. Pipette 12M HCl (in a fume hood) into the tube to shift equilibrium to the right (blue).
3. Add water to shift equilibrium back left (pink).
4. Heat the tube in a hot water bath to shift equilibrium to the right (blue).
5. Place in an ice water bath to shift back to the left (pink).
6. Add a bit more HCl to shift back to right (blue).
7. Add 1M  $\text{AgNO}_3$  to precipitate  $\text{AgCl}$  and shift equilibrium back to the left (pink).
8. Pour supernatant into waste container and rinse precipitate thoroughly with water.
9. Dissolve the precipitate in concentrated  $\text{NH}_3$  (in a fume hood, probably could use 6M)

I discuss the equilibrium shift qualitatively. It also allows for discussion on why the equilibrium constant changes with temperature, introduces complex ions, and gives a preview to solubility equilibria.



④

$$K_{eq} = \frac{(0.202)^2}{(0.399)(0.197)^3} = 5.96 \times 10^{-2}$$

$$K > Q$$

the  $E_q$  must shift Right.

$$Q = \frac{(0.202)^2}{(0.399+1.00)(0.197)^3} = 1.70 \times 10^{-2}$$

## Effect on $E_q$

### 3 ways to effect P

1. Add or Remove gaseous product/reactant - Been done

2. Add inert gas (not involved in Rxn) → No effect only ~~those~~ things that are with  $E_q$  affect the  $E_q$

3. Change Volume of Container

↳ ~~If  $P$  or  $Q$  changes~~, If  $V$  changes,  $[ ]$ 's but the system responds to decrease  $[ ]$  by going to the fewest gas molecules present.

13.14 page 608

## Temp Effect $E_q$

$K$  changes w/ Temp But LeChatlier's principle can be used



If  $T \uparrow$ ,  $E_q$  shifts in direction that consumes  $E$  making  $K \downarrow$

If  $T \downarrow$   $E_q$  shifts → and  $K \uparrow$   
opposite for Endothermic Rxn.